



Effect of the reducing agent on the hydrodechlorination of dioxins over 2 wt.% Pd/ γ -Al₂O₃

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ABSTRACT

2-Propanol and molecular H₂ (in methanol (MeOH) and MeOH–water) were examined as reducing agents for the liquid phase hydrodechlorination (HDC) of dioxins over 2 wt.% Pd/ γ -Al₂O₃. Different amounts of NaOH were added to the reaction mixtures. The 2-propanol and H₂(g)/MeOH systems presented similar HDC activity. Notwithstanding, Pd sintering and graphitic carbon directly bonded to Pd on catalyst surface was observed on samples used with H₂(g)/MeOH. The addition of water to H₂(g)/MeOH decreased Pd sintering and favored dissolution of sodium compounds. However, dioxin degradation efficiency diminished. By contrast, 2-propanol acting both as reducing agent and solvent provided hydrogen to the HDC reaction, avoided metal sintering and Pd–C formation. Besides, almost complete dioxin degradation under mild reaction conditions was obtained. Kinetic experiments of dioxin HDC with 2-propanol showed a maximum net reaction rate and turnover frequency (TOF) for a given initial concentration of polychlorinated dibenz-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). After that value, both reaction rate and TOF decreased. On the other hand, reaction rates and TOFs of dioxin-like polychlorinated biphenyls (DL-PCBs) linearly increased with concentration.

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1. Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are a group of structurally related chemicals which persist in the environment, bioaccumulate in the food chain and are toxic. These compounds have similar mechanisms of toxicity so they are grouped together when considering potential risks [1]. Congeners containing chlorine at 2,3,7,8 positions have been identified as more toxic to exposed organisms. So, target substances are reduced to 7 PCDDs and 10 PCDFs. Nevertheless, not all 2,3,7,8 chlorinated PCDDs/PCDFs have the same toxicity. The most toxic is considered to be 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) [1]. Although there are far fewer data on the other sixteen 2,3,7,8-substituted compounds, dioxins are found in the environment as complex mixtures, and it is necessary to have some way of assessing the toxicity of such mixtures. The World Health Organization (WHO) defined the toxic equivalence factors (TEF) to measure the concentration of dioxins and furans in terms of the overall toxicity of the mixture [2]. The concentration of either compound is multiplied by its corresponding TEF giving the toxic equivalent concentration (TEQ). The sum of

all TEQs provides the amount of 2,3,7,8-TCDD that gives the same overall toxic effect. The close toxicological similarity of coplanar polychlorinated biphenyls (PCBs) to dioxins has led to the extension of the TEF system to some of the coplanar PCB compounds, the dioxin-like PCBs, and for the TEQ of an environmental sample to include contributions from dioxins, furans and dioxin-like PCBs. In 1997, the WHO system of TEFs includes TEF values for 12 non-ortho- and mono-ortho-PCBs that have demonstrated dioxin-like toxicity [2].

Waste incineration is an important source of dioxins, furans and dioxin-like PCBs which are mainly concentrated in the solid residues of gas cleaning systems [1,3,4]. Actions for suitable treatment and inertization of solid waste, in particular fly ash, are of primary concern because improper disposition of this waste can lead to severe environmental pollution [5]. HDC is one of the most promising methods for detoxifying chlorinated organic waste [6]. As a non-destructive approach, HDC represents a complement to the traditional landfill disposal of solid waste because it can reduce sample toxicity under mild conditions avoiding future environmental contamination. Nevertheless, a large variety of chlorinated compounds with different toxicity and degradation pathways make HDC of real fly ash samples a complex technique affected by several parameters. Particularly, PCDD/Fs degradation is the main target in fly ash HDC studies, due to their important contribution to total sample toxicity, stable chemical structure, trace concentration in

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environmental samples, and interference with other coexistent halogenated pollutants at higher concentrations [5]. Additionally, dioxin degradation might indicate destruction of other chlorinated hydrocarbons from fly ash.

The source of hydrogen for HDC can be either molecular hydrogen or a hydrogen donor [7]. HDC of PCDD/Fs fly ash extracts with molecular hydrogen over a supported metal catalyst (Pt/C or Pd/C) was successfully accomplished in a multiphase reaction system (isooctane–water) [8]. PCDD/Fs and DL-PCBs from fly ash samples collected from a commercial solid-waste incinerator were HDC at 355 K over 5 wt.% Pd/Al₂O₃ using 2-propanol as solvent and hydrogen source [9]. Comparable results were obtained over 2 wt.% Pd/γ-Al₂O₃ [10]. Dioxin HDC reactions over Pd/C have been recently reported by Yang et al. [5] using a 2-propanol/water solution and by Zhang et al. [11] using a H₂(g)/ethanol/water mixture. These systems provided complete dioxin degradation at temperatures below 323 K. Additionally, methanol/water and ethanol/water mixtures demonstrated superior efficiency compared to pure methanol or ethanol for the HDC of tetrachloroethylene [12,13], chlorophenols [14], and aromatic halides [15] over Pd/C. In this work, 2-propanol and molecular H₂ (in MeOH and MeOH/water) were examined as reducing agents for the HDC of dioxins over 2 wt.% Pd/Al₂O₃. Reactions were carried at the solvent boiling points and different NaOH amounts were added. Fresh and used catalyst samples were characterized by TEM-EDS, XPS, XRD and TGA/DTA. Also, the effect of the initial concentration on the HDC rate of dioxins was evaluated in the 2-propanol/2 wt.% Pd/γ-Al₂O₃/NaOH system.

2. Experimental

2.1. Materials

Palladium acetylacetonate (99%, Aldrich Chem. Co., USA) was used as Pd precursor and γ-alumina (99.97%, Alfa Aesar, USA) as support material. All solvents used for catalytic tests and PCDD/Fs extraction, clean up and analysis were Ultimic Grade from Mallinckrodt Baker (USA). Silica, florisil and alumina adsorbents for cleaning up were from Merck, Germany. EPA-1613CVS (CS1–CS5) calibration solutions, EPA-1613LCS extraction standard and EPA-1613ISS syringing standard for PCDD/Fs determination were obtained from Wellington Laboratories (Canada). All ultra-high purity gases were purchased from AGA, Colombia.

2.2. Catalyst preparation

2 wt.% Pd/γ-Al₂O₃ was prepared by wetness impregnation. The amount of palladium acetylacetonate necessary to obtain 2 wt.% Pd loading was dissolved in 10–20 mL of acetone. This mixture was slowly added to γ-alumina under continuous stirring at 313 K allowing acetone evaporation. The resulting solid was oven dried at 373 K during 12 h. The catalyst was pretreated at 2 K min⁻¹ up to 673 K for 1 h in flowing 50 mL min⁻¹ air and reduced at 2 K min⁻¹ up to 573 K in 50 mL min⁻¹ flowing 10% H₂/N₂. The samples were maintained at this temperature for 1 h. Finally, they were cooled down to room temperature in flowing nitrogen. Calcined and reduced catalyst samples were coded as PA-act. Pd dispersion of the PA-act samples was 21.3% as previously reported [16].

2.3. Catalytic tests

Fly ash samples were taken from a container filled with accumulated bag filter fly ash from several incineration batches of an incinerator located in Medellin, Colombia. Solid samples were soxhlet extracted with toluene during 48 h. One fraction of the liquid extract was cleaned up and analyzed following EPA1613

method as described previously [10,18]. Briefly, fly ash extract samples were spiked with EPA1613-LCS standard and cleaned up. Cleaned samples were analyzed by high resolution gas chromatography coupled to ion-trap low resolution mass spectrometry (HRGC-QITMS/MS) in a Varian CP-3800 GC coupled to a Saturn 2000 ion-trap spectrometer equipped with an 8400 auto sampler and a DB-5MS column (60 m × 0.25 mm I.D., 0.25 μm film thickness). Quantification of dioxins, furans and DL-PCBs were performed by the isotope dilution method. Relative response factors (RRFs) were determined using calibration standards for PCDD/Fs and DL-PCBs analysis (EP1613-CS and WP-CS solutions from Wellington Labs, Canada). Toxic equivalents (WHO-TEQ) were determined using WHO-TEF factors [10,18]. The detection limit of 2378-TCDD was 8.22E–12 g.

HDC reactions were performed in three mouth round bottom flasks equipped with a septum, a thermowell and a condenser. When 2-propanol was the reducing agent, reaction mixtures consisted of 400–600 μL of fly ash extracts dissolved in toluene at different initial dioxin concentrations, 100 mg of 2 wt.% Pd/γ-Al₂O₃ and different amounts of NaOH dissolved in 20 mL of 2-propanol. The fly ash extract samples were coded as S10, S50, S75, S150 and S250 depending on the initial ng TEQ added to the reaction mixture, i.e. S10 corresponds to the addition of 10 ng TEQ. On the other hand, when molecular hydrogen was the reducing agent MeOH and 20–80% MeOH–water mixtures were used as solvents. 75 ng TEQ (S75) was used in these experiments. At the beginning of the reaction molecular hydrogen was injected several times into the system through a septum and kept at a slightly higher pressure than atmospheric. Then, the reaction mixture was heated to the desired temperature. The reaction temperature varied depending on the solvent boiling point, i.e. 333 K for MeOH or 348 K for 2-propanol.

As we previously reported [10], the absence of mass transfer limitations was confirmed using different catalyst particle diameters and checking the compliance to Koros–Nowak criterion at 2300 rpm stirring velocity [19,20]. The sieve fraction used was lower than 37 μm (400 mesh). After a 3-h reaction, the catalyst was recovered by filtration, washed with 100 mL of toluene and dried at 373 K during 24 h. Used catalyst samples were coded as PA-X-Y, where X denotes the reducing agent, i.e., 2P for 2-propanol and H₂ for molecular hydrogen and Y denotes the reaction temperature in Kelvin.

The HDC over 2 wt.% Pd/γ-Al₂O₃ of toxic compounds, i.e. 7 dioxins, 10 furans and 12 PCBs, was determined by calculating the conversion of either toxic compound from its concentration in the sample before and after reaction. Also, total conversion (TC %) was figured out by summing up the conversion of all toxic compounds before and after reaction (Eq. (1)) and the percent toxicity reduction (TR %) was obtained from the initial and final ng TEQ of each sample (Eq. (2)) [10].

$$TC(\%) = \frac{\sum_{1}^{29} [PCDD/PCDF/PCB]_{initial} - \sum_{1}^{29} [PCDD/PCDF/PCB]_{final}}{\sum_{1}^{29} [PCDD/PCDF/PCB]_{initial}} \quad (1)$$

$$TR(\%) = \frac{(ng\ TEQ)_{initial} - (ng\ TEQ)_{final}}{(ng\ TEQ)_{initial}} \quad (2)$$

When 2-propanol was used as reductant, the turnover frequency (TOF) was calculated taking Pd dispersion as 21.3% [19] and the Pd loading listed in Table 2. The production of hydrogen was estimated from the amount of acetone generated in the reaction mixture after 30-min reactions at different temperatures, in the presence and in the absence of dioxin extracts. From stoichiometry 1 mol of 2-propanol produces 1 mol of acetone and 1 mol of H₂ [21,22]. After reaction, the sample was cooled down to room

temperature and a liquid fraction analyzed for 2-propanol and acetone in an Agilent 7890A GC equipped with a TCD detector and a CarboWax column, 30 m, I.D. 0.32 mm (Agilent, USA).

The mole fraction of dissolved H₂ in methanol was estimated from the Henry's law (Eq. (3)) [23]:

$$x_2 = \frac{\bar{P}}{H_2^\infty} \quad (3)$$

where \bar{P} is the partial pressure of H₂ and H_2^∞ is the Henry's law constant. Since solubility data are generally reported at 101.3 kPa, all the calculations were made assuming this partial pressure of H₂. H_2^∞ was calculated using the empirical correlation proposed by Descamps et al. [23] for H₂ in methanol (Eq. (4)). They reported an uncertainty of about $\pm 10\%$ for this equation.

$$\ln H_2^\infty = 19.7009 + \frac{1.7329}{\tau} + 0.6885 \ln(T) - 0.0116T \quad (4)$$

where T is expressed in Kelvin. The solubility of H₂ in MeOH/H₂O mixtures was calculated from Eq. (5) proposed by O'Connell and Prausnitz [24]:

$$\ln x_{H_2, \text{mixture}} = \phi_{\text{MeOH}} \ln x_{H_2, \text{MeOH}} + \phi_{H_2\text{O}} \ln x_{H_2, \text{H}_2\text{O}} + a_{\text{MeOH}/\text{H}_2\text{O}} \phi_{\text{MeOH}} \phi_{H_2\text{O}} \quad (5)$$

where ϕ represents the volume fraction of the two solvents and $a_{\text{MeOH}/\text{H}_2\text{O}}$ describes the interaction between the two solvents. This parameter was taken as zero assuming ideal solution. Less than 10% error between observed and predicted values was reported by Purwanto et al. [25] for the H₂/ethanol/water system under the assumption of ideal solution.

The solubility of H₂ in water at 101.3 kPa was estimated using the equation proposed by Fogg and Gerrard [26]:

$$\ln x = A + \frac{B}{\tau} + C \ln T + DT \quad (6)$$

which is valid in the temperature range 173–345 K with $A = -125.939$, $B = 5528.45$, $C = 16.8893$, $D = 0$ and T (K).

2.4. Catalyst characterization

Elemental analysis was performed by atomic absorption in a Philips PU9200 apparatus. Transmission electron microscopy (TEM) experiments were carried out in a JEOL JEM-2010 microscope operating at 200 kV coupled to an X-ray energy dispersion spectroscope (EDS) OXFORD instruments model INCA Energy TEM100 with a Si(Li) detector, 30 mm² of detection area and resolution of 142 eV. Samples were dispersed in ethanol by ultrasonic vibration and dropped on a copper grid coated with carbon film. At least 200 individual Pd particles were counted for either catalyst sample and the mean Pd particle size was given as the surface-area-weighted average size ($\bar{d}\text{Pd}$) [6,17].

XPS spectra were obtained in a VG-Microtech Multilab electron spectrometer using the Mg K α (1253.6 eV) radiation of twin anode in the constant analyzer energy mode with pass energy of 50 eV. The analysis chamber was maintained at 5.10E–10 mBar. The Al 2p line at 74.2 eV was used as a reference together with the C 1s line at 284.6 eV. The accuracy of BE values was ± 0.2 eV. The BE values were obtained by using the Peak-Fit Program implemented in the control software of the spectrometer.

X-ray diffraction was performed using a Bruker D8-Advance diffractometer with an X-ray generator Kristalloflex K 760-80F (output: 3000 W, voltage: 20–60 kV and stream: 5–80 mA) with K α radiation (1.5406 Å), $2\theta = 2\text{--}80^\circ$. Database JCPDS was used for analyzing results. TGA/DTG was carried out in a TA instrument Q500. Around 10 mg of catalyst sample was heated in air at 100 mL min⁻¹. Samples were outgassed for 1 h at 298 K and heated at 5 K min⁻¹ until 1073 K.

3. Results and discussion

3.1. Catalytic tests

Table 1 lists results of 3-h reactions at different NaOH concentrations and temperatures. Three NaOH concentrations were tested: 12.5, 37.5 and 62.5 mM. As can be observed in Table 1 when the concentration of NaOH was 37.5 mM a high total conversion and toxicity reduction was obtained in both systems: 2-propanol (348 K) and H₂(g)/MeOH (333 K). After reaction the pH was almost 12 in both systems indicating that this amount of NaOH (37.5 mM) was in considerable excess relative to the amount of theoretical HCl in the reactor. The HDC mechanism of 1234-TCDD over Pd catalyst was studied by Ukius and Miyadera [27] using deuterium-labeled 2-propanol and found that the α -hydrogen of 2-propanol preferentially transferred in the form of a hydride species to the organic chlorines on the catalyst surface. Kopinke et al. [28] found that under alkaline conditions this is the dominant HDC mechanism. So the NaOH effect might be twofold: neutralize released HCl and maintain the alkalinity of the system. However, further increase to 62.5 mM NaOH decreased toxicity reduction. Therefore, the NaOH concentration should not be too high as to poison the catalyst by Na deposits [16,28]. Results in Table 1 indicate that the H₂ saturated methanol solvent was more affected than 2-propanol when 62.5 mM NaOH was used. This behavior can be linked to the temperature effect on NaOH solubility at the reaction temperature (333 K for H₂(g)/MeOH and 348 K for 2-propanol). The lower the reaction temperature, the lower the NaOH solubility and more inorganic deposits are expected on catalyst samples used in the H₂(g)/MeOH system, *vide infra*.

Several studies have shown that methanol cannot only act as a solvent but also as a hydrogen donor [29]. When methanol was used as reductant at a NaOH concentration of 37.5 mM (Table 1)

Table 1
Total conversion and toxicity reduction of PCDD/Fs extracts after a 3-h hydrodechlorination reaction.

Reducing agent	NaOH (mM)	Temperature (K)	Total conversion (%)	Toxicity reduction (%)
2-Propanol	12.5	348	99.83	98.72
	37.5	348	99.70	99.59
	62.5	348	99.68	98.55
	37.5	338	81.35	59.31
	37.5	328	44.85	39.06
H ₂ (g)	12.5	333	89.15	74.41
	37.5	333	94.24	87.02
	62.5	333	57.54	32.84
Methanol	37.5	333	68.31	Toxicity increased by 21.92%

Reaction conditions: 75 ng TEQ, 100 mg of 2 wt.% Pd/ γ -Al₂O₃ in 20 mL of either 2-propanol or methanol.

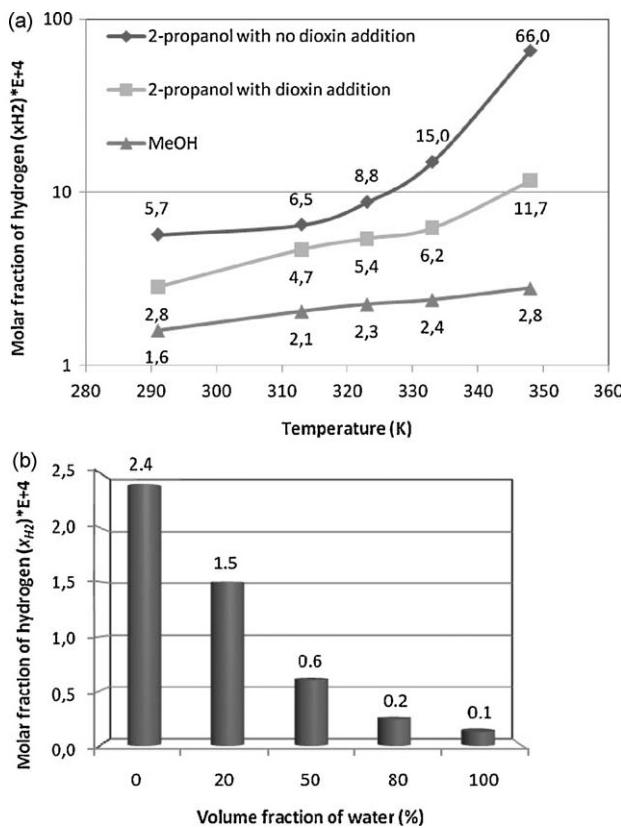


Fig. 1. Molar fraction of hydrogen in the liquid phase (a) in 2-propanol and H₂(g)/MeOH systems at several temperatures and (b) in H₂(g)/MeOH/H₂O mixtures at 333 K.

the total conversion was 68%. Notwithstanding, the toxicity of the mixture increased by about 22% due to dechlorination of more chlorinated congeners which increased the concentration of less chlorinated i.e. more toxic ones. The high reactivity of more chlorinated compounds has been previously reported even in the absence of catalyst [9,16]. Therefore, under the conditions of this study, MeOH was found to be a less efficient hydrogen source than 2-propanol for the complete degradation of dioxin extracts.

The lower efficiency of methanol as reducing agent for dioxin HDC over 2 wt.% Pd/ γ -Al₂O₃ is ascribed to Pd sintering and carbon deposition as will be shown *vide infra*. Studies by in situ vibrational sum frequency generation (SFG) and X-ray photoelectron spectroscopy (XPS) provided by Morkel et al. [30] confirm our results. They examined two competing methanol decomposition pathways on Pd(1 1 1), i.e., dehydrogenation of CH₃OH to CO and H₂ and methanolic C–O bond scission. Pd(1 1 1) was found to be quite active for methanolic C–O bond scission. The CH_x formation rate strongly increased with pressure and temperature, leading to immediate catalyst deactivation at 0.1 mbar and 400 K. Complete dehydrogenation of CH_x species and partial dissolution of atomic carbon in the Pd bulk most likely occurred even at 300 K.

Fig. 1 shows the estimated molar fraction of hydrogen in the liquid phase at several temperatures in the 2-propanol, H₂(g)/MeOH and H₂(g)/MeOH/H₂O systems. x_{H_2} in MeOH and MeOH/H₂O mixtures was calculated from solubility data. x_{H_2} in the 2-propanol system was estimated by measuring acetone production over 2 wt.% Pd/ γ -Al₂O₃ catalyst after 30-min reactions both in the presence and in the absence of dioxins. The diminished H₂ production in the 2-propanol system in the presence of dioxins suggests competitive adsorption over Pd/ γ -Al₂O₃. The production of hydrogen vs temperature in the 2-propanol system increased more than 10 times in the absence of dioxins and more than 4

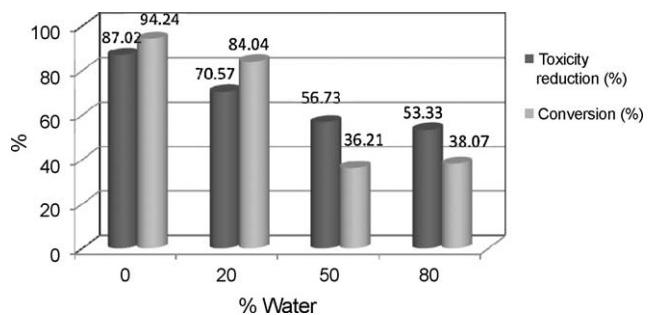


Fig. 2. Effect of water on the HDC of PCDD/Fs after 3-h HDC reactions using H₂ as reducing agent. Reaction conditions: 100 mg of 2 wt.% Pd/ γ -Al₂O₃ and 75 ng TEQ of PCDD/Fs in 20 mL of MeOH or MeOH/H₂O mixtures and 37.5 mM NaOH at 333 K.

times in their presence. This might explain the important effect of the reaction temperature on the total conversion of dioxins in the 2-propanol system (see Table 1). In contrast, the solubility of hydrogen in methanol appears to be less affected by temperature (see Fig. 1a). Besides, the molar fraction of H₂ in methanol/water mixtures decreased with water content (see Fig. 1b) leading to less hydrogen available for the HDC reaction.

Water has been added to MeOH or EtOH solvents during the hydrodechlorination of dioxins [11,31], tetrachloroethylene [12,13], chlorophenols [14] and aromatic halides [15] over Pd/C using hydrogen as reducing agent. The aqueous medium decreased the formation of catalyst solid deposits retarding its deactivation. In the present study, different amounts of H₂O were added into the H₂(g)/MeOH system to assess their effect on dioxin degradation over 2 wt.% Pd/Al₂O₃. As shown in Fig. 2, the presence of water has a negative effect on the degradation of PCDD/Fs over 2 wt.% Pd/Al₂O₃. This result may be ascribed to the weak chemical affinity of hydrated Al₂O₃, at a pH over the isoelectric point (7–8), to hydrocarbons [32]. However, Pd sintering and Na deposits were avoided in the presence of water, *vide infra*.

3.2. Catalyst characterization

3.2.1. Chemical analysis and X-ray photoelectron spectroscopy (XPS)

Table 2 lists Pd loading of catalyst samples before (PA-Act) and after HDC reactions. Differences in Pd loading between fresh and used samples were lower than 0.2% and no important effects of the solvent were observed. C 1s, Pd 3d and Na 1s binding energies (B.E.) and percent atomic ratios are also listed in Table 2. A C 1s peak around 284.5 eV displayed in all catalyst samples is attributed to adventitious carbon (AC) that corresponds to adsorbed species typically present in samples after exposure to ambient air [33–36]. Fresh samples display a small C 1s feature at 286.6 eV ascribed to highly oxidized carbon species bonded to oxygen. This C–O species is linked to residues from Pd precursor (palladium acetylacetone) [33,37,38]. PA-2P-348 exhibits a C 1s peak about 285.1 eV ascribed to C–OH species [35]. Catalysts samples used with H₂ as reducing agent exhibit carbon species with B.E. lower than 283.7 eV ascribed to negatively charged carbon species directly bonded to palladium [35]. This species has been associated with a form of atomic carbon such as C_{ads} on various surfaces (283.7 eV on Rh, 283.8 eV on Fe, 282.9 eV on Pd), as reported by Ahn et al. [35].

B.E. values of Pd 3d_{5/2} listed in Table 2 indicate that fresh catalyst samples (PA-Act) were completely reduced during the activation process [33–42]. All used catalyst samples contain reduced Pd with B.E. between 334 and 335 eV [34–42]. Na 1s with B.E. over 1071 eV ascribed to NaCl species were detected on samples PA-2P, PA-H₂ and PA-H₂ (20% H₂O) [37,41,42]. However, in the presence of large amounts of H₂O, NaCl was not detected in PA-H₂.

Table 2

Pd loading, binding energies (eV) and atomic concentration (at.%) of fresh and used 2 wt.% Pd/ γ -Al₂O₃ samples.

Catalyst	Pd loading (%) ^a	Binding energies (eV) ^b			Atomic ratio (at.%) ^b		
		C 1s	Pd 3d _{5/2}	Na 1s	C/Al	Pd/Al	Na/Al
PA-act	1.94	284.6; 286.6	334.2	N.D. ^c	29.00	0.90	0.00
PA-2P-348	1.90	284.0; 285.1	335.0	1071.1	71.53	0.92	13.00
PA-H ₂ -333	2.04	283.7; 285.0	334.1	1071.2	53.22	0.88	10.13
PA-H ₂ -333 (20% H ₂ O)	1.74	283.6; 284.9	334.3	1071.8	65.32	0.98	8.54
PA-H ₂ -333 (50% H ₂ O)	2.00	282.4; 284.3	335.0	N.D. ^c	113.44	0.74	0.00
PA-H ₂ -333 (80% H ₂ O)	1.83	283.1; 284.5	334.9	N.D. ^c	56.63	1.35	0.00

^a Measured by atomic absorption.

^b From XPS analyses.

^c N.D., not detected.

3.2.2. Transmission electron microscopy (TEM)

TEM images (Fig. 3) illustrate the effect of 2-propanol and H₂(g)/MeOH on Pd morphology after a 3-h reaction. Fresh catalyst samples (PA-act) and those used with 2-propanol (PA-2P) show

well dispersed and homogeneous Pd particles, as can be confirmed from particle size distribution and *d* values displayed in Fig. 4. In agreement with our previous results, when 2-propanol was used as reducing agent no changes of the catalyst active phase after

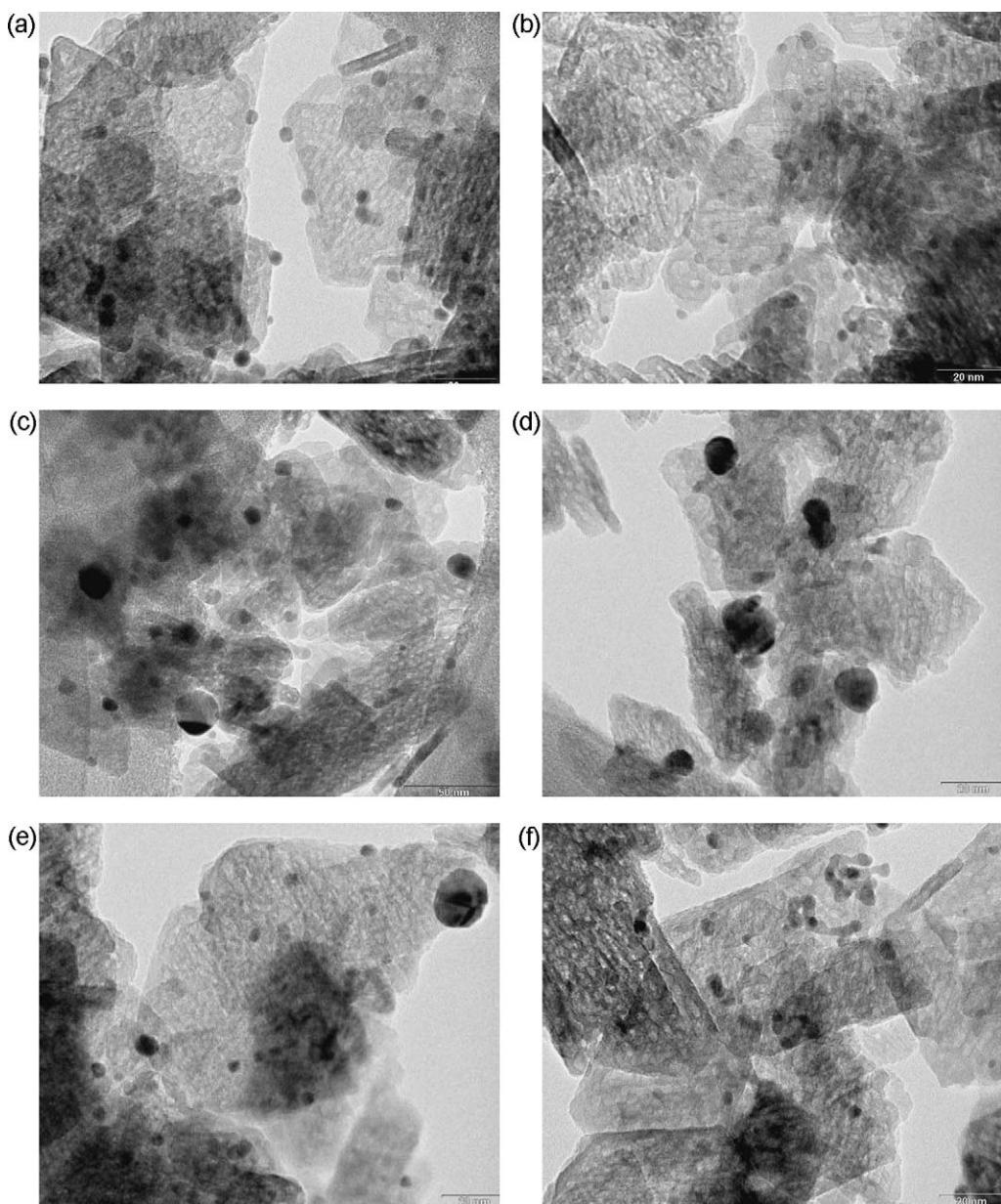


Fig. 3. TEM images of 2 wt.% Pd/ γ -Al₂O₃ samples: (a) fresh catalyst after calcination and reduction (PA-act), (b) used in a 3-h HDC reaction with 2-propanol at 348 K (PA-2P-348), (c) used in a 3-h HDC reaction with H₂(g)/MeOH at 333 K (PA-H₂-333), (d) PA-H₂-333(20% H₂O), (e) PA-H₂-333 (50% H₂O) and (f) PA-H₂-333 (80% H₂O).

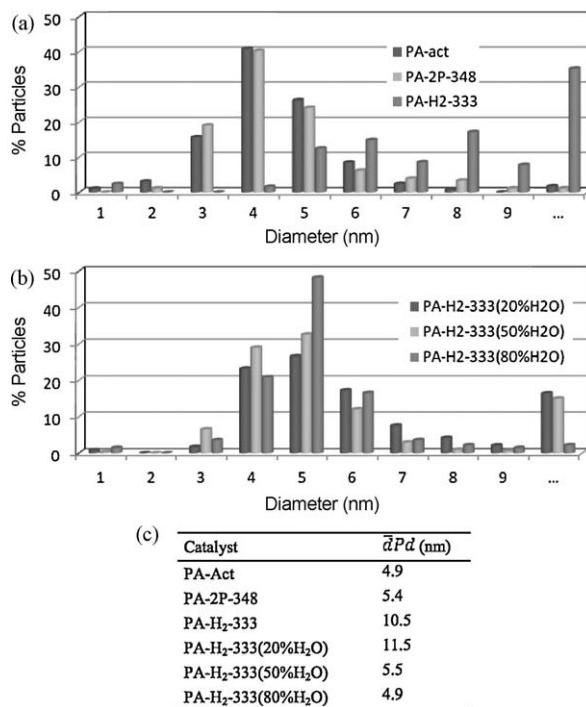


Fig. 4. Particle size distribution of 2 wt.% Pd/ γ -Al₂O₃ samples (a) fresh (PA-act) and used after a 3-h reaction with different reducing agents and (b) used with molecular hydrogen and several MeOH/H₂O ratios. (c) Pd surface area weighted average size.

reaction are observed neither in size nor in morphology [16]. In contrast, increasing of Pd average size was found for PA-H₂-333 used in MeOH solvent (Figs. 3c and 4a). Several authors have reported a negative effect of high methanol concentrations on Pd catalyst samples for HDC reactions [13]. Although this effect has been associated with catalyst deactivation by NaCl and carbon deposits, the present results show that this medium also promotes Pd sintering. Ukisu [43] reported HDC improvements of p-chloroanisole, 2-chloronaphthalene, and (2-chloroethyl) benzene over Pd catalysts in a 2-propanol:methanol (99:1, v/v) mixture but increasing methanol concentration lowered the dechlorination rate. He ascribed the positive effect of low methanol concentrations to a possible promotion of the hydrogen-transfer reaction on catalyst surface. Nevertheless, these phenomena are not yet well

understood [43]. Bimetallic supported catalysts based on nanoparticles of Pd–Zn and Pd–Fe alloys show higher stability in the presence of methanol. Pd–Zn/Al₂O₃ has been successfully tested for the steam reforming of methanol [40,44], and Pd–Fe for the HDC of trichloroethylene [45]. Alloys diminished Pd agglomeration on the catalyst surface.

Although Pd chains were observed, TEM images (Fig. 3d–f) revealed particle size decrease by increasing water concentration. As the addition of water increased, particle size and Pd distribution approached the values of fresh catalyst samples. When 80% H₂O was added, d decreased until 5.5 nm and almost 50% of particles were within 5–6 nm (Fig. 4). So, the strong Pd sintering promoted by methanol was reduced by water addition. Only water was used as solvent for the HDC of 4-chlorophenol over Pd/C reaching complete degradation [14]. Carbon has low affinity for water, so it may preferentially adsorb components from aqueous solutions. However, as discussed above, the lower H₂ solubility in water and the low affinity of alumina (above the isoelectric point) to hydrocarbons limit the use of this solvent when the dioxin HDC is carried out over Pd/ γ -Al₂O₃.

3.2.3. X-ray diffraction (XRD)

X-ray diffraction patterns (not shown) of fresh and used catalyst samples exhibited characteristic peaks of γ -Al₂O₃ around $2\theta = 38.0^\circ, 44.3^\circ, 47.3^\circ$ and 65.3° [9,46–49]. Peaks corresponding to palladium (Pd: $2\theta = 40^\circ, 47^\circ$ and PdO: $2\theta = 34^\circ, 55^\circ, 60^\circ$) were not detected by XRD suggesting that Pd (2 wt.%) was highly dispersed [9,16]. A peak at $2\theta = 54.2^\circ$ ascribed to graphitic carbon was detected in catalyst samples used in MeOH and MeOH/water (PA-H₂). This species is avoided or diminished in the presence of 2-propanol as reducing agent.

3.2.4. TGA

TGA and DTG results of fresh and used samples of 2 wt.% Pd/ γ -Al₂O₃ are listed in Table 3. Fresh samples (PA-Act) did not exhibit remarkable weight loss up to 800 °C. DTG curves exhibited several peaks associated with the elimination of different compounds from used catalyst samples. The weight loss between 298 and 422 K (ΔT_1) has been associated with the loss of moisture and loosely bound reactants [39,50]. Marécot et al. [51] established oxidation temperatures between 473 and 873 K for carbonaceous deposits on Pd/SiO₂ catalysts. By TPO and FTIR they found that carbon desorption at 523 K corresponds to coke deposited on the (1 1 1) Pd planes whereas the peak at ca. 473 K involves palladium atoms of

Table 3

Weight loss and oxidation temperature of fresh and used 2 wt.% Pd/ γ -Al₂O₃ samples.

Catalyst sample	Weight loss (%)			Oxidation temperature (K)		
	$W(\Delta T_1^a)$	$W(\Delta T_2^b)$	$W(\Delta T_3^c)$	T_1	T_2	T_3
Effect of the reducing agent						
PA-Act	2.27	1.00	0.77	–	–	–
PA-2P-348 ^d	2.31	6.91	3.19	354	531	702
PA-H ₂ -333 ^d	2.75	3.61	2.60	303	592	726
PA-H ₂ -333 (20% H ₂ O) ^d	0.80	4.65	2.18	330	578	721
PA-H ₂ -333 (50% H ₂ O) ^d	1.77	2.49	2.76	312	587	721
PA-H ₂ -333 (80% H ₂ O) ^d	2.39	4.10	2.09	304	584	689
Effect of the initial TEQ						
PA-2P-348 [S10] ^e	1.89	4.11	1.32	323	491	683
PA-2P-348 [S150] ^e	2.11	5.92	2.05	311	508	682
PA-2P-348 [S250] ^e	1.94	7.27	2.19	318	527	683

^a $\Delta T_1 = 298–422$ K.

^b $\Delta T_2 = 423–652$ K.

^c $\Delta T_3 = 653–1073$ K.

^d Reaction conditions: 100 mg of 2 wt.% Pd/ γ -Al₂O₃ and 75 ng TEQ in 20 mL of 37.5 mM NaOH in either 2-propanol (2-propanol as reductant) or methanol or methanol–water mixtures (H₂(g) as reductant) after 3-h HDC reaction at several reaction temperatures.

^e Reaction conditions: 100 mg of 2 wt.% Pd/ γ -Al₂O₃ and several initial TEQ in 20 mL of 37.5 mM NaOH in 2-propanol at 348 K after 1-h HDC reaction.

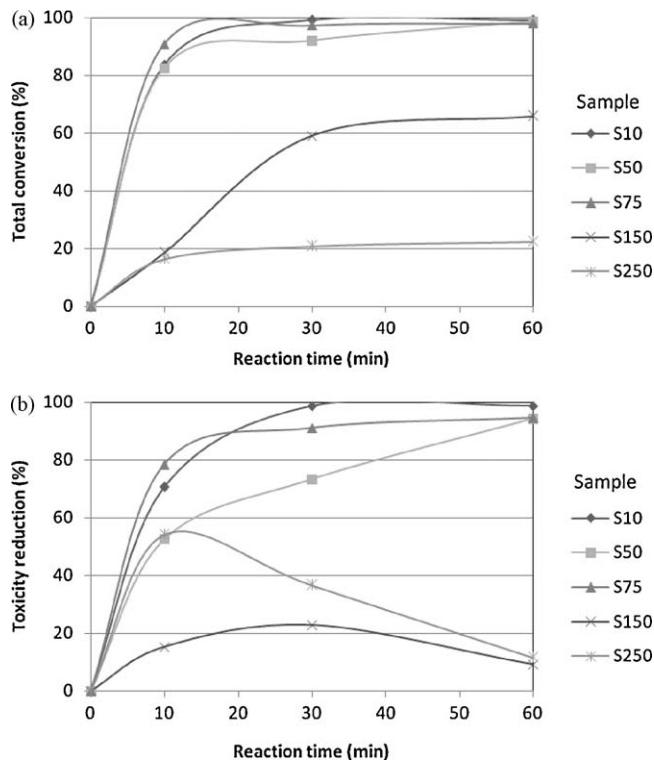


Fig. 5. Total conversion (a) and toxicity reduction (b) over 2 wt.% Pd/γ-Al₂O₃ using reaction mixtures with different initial dioxin concentrations. Reaction conditions: 100 mg of 2 wt.% Pd/γ-Al₂O₃ catalyst in 20 mL of 2-propanol and 37.5 mM NaOH at 348 K.

lower coordination number like corners, edges or (1 0 0) Pd planes [51]. In order to evaluate both peaks separately, the weight loss in the 423–652 K (ΔT_2) and 653–1073 K (ΔT_3) ranges was calculated for each kind of deposited carbon (see Table 3). Weight loss at low temperatures was similar for fresh and used catalyst samples when 2-propanol and H₂(g)/MeOH were used as reductants. Differences in oxidation temperatures are attributed to differences in the solvent boiling points and catalyst affinity. In ΔT_2 and ΔT_3 zones, PA-2P showed the greatest weight loss associated with the lower combustion temperature. In agreement with XPS results, the carbonaceous residues over PA-2P catalyst can be mainly associated with C-OH species. In contrast, carbon deposition (Pd-C) above 573 K on PA-H₂ catalyst samples (see Table 3) confirms its higher stability.

3.3. Dioxin HDC over 2 wt.% Pd/γ-Al₂O₃ using 2-propanol as reducing agent

Under the conditions of this study, 2-propanol was found to be an efficient hydrogen source providing a stable environment to the catalyst and avoiding the use of molecular hydrogen. Therefore, the effect of the initial concentration of dioxins on the reaction rate of the toxic congeners, i.e. 7 dioxins, 10 furans and 12 DL-PCBs was evaluated. Fig. 5 shows total conversion and toxicity reduction vs time for HDC of fly ash extract samples over 2 wt.% Pd/γ-Al₂O₃. The degradation system appears to be effective for dioxin degradation when low initial concentrations are used. If the initial TEQ is raised to 150–250 ng, the degradation is drastically reduced. The HDC of real samples contaminated with dioxins involves the transformation of more to low chlorinated congeners. Thus, dioxin hydro-dechlorination reactions can be expressed as:

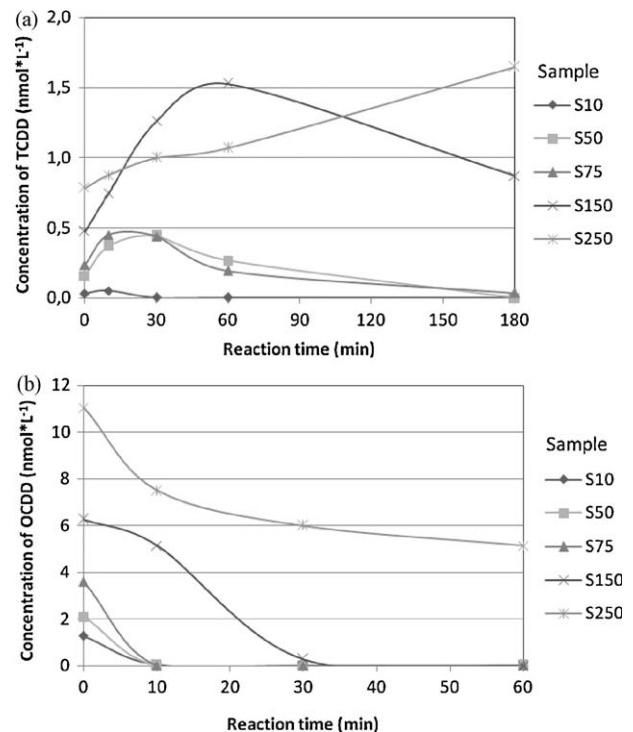
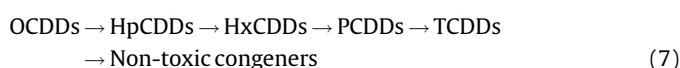


Fig. 6. Concentration of (a) 2,3,7,8-TCDD and (b) OCDD vs time during dioxin HDC over 2 wt.% Pd/γ-Al₂O₃ using reaction mixtures with different initial dioxin concentrations. Reaction conditions: 100 mg of 2 wt.% Pd/γ-Al₂O₃ catalyst in 20 mL of 2-propanol and 37.5 mM NaOH at 348 K.



$$\rightarrow \text{Non-toxic congeners} \quad (8)$$



Complete degradation of dioxin congeners occurs by consecutive reactions where the net reaction rate of each compound can be expressed as follows:

$$r_{A,\text{Net}} = r_{A,\text{formation}} + r_{A,\text{dechlorination}} \quad (10)$$

where $r_{A,\text{formation}}$ is positive and $r_{A,\text{dechlorination}}$ is negative.

Fig. 6 shows the effect of the number of chlorine atoms in the starting molecule on the concentration vs time profile. A parabolic profile with a peak maximum was found for less chlorinated compounds like TCDD (Fig. 6a) because at short reaction times the formation was faster than the dechlorination. In contrast, the concentration of more chlorinated compounds, as OCDD (Fig. 6b) decreased with time. In order to compare the degradation efficiency at different initial pollutant concentrations, the initial net reaction rate for each compound was determined from the concentration vs time curve. The net reaction rate for those compounds exhibiting a parabolic concentration profile was estimated when the concentration started to decline. Fig. 7 shows the net reaction rates and Table 4 list the turnover frequencies (TOF) of PCDD/Fs and DL-PCBs congeners at different initial concentrations. Higher reaction rates and TOFs were observed for furans compared to both dioxins and DL-PCBs, especially for 1234678-HpCDF which has TOF of 1.9E-7 s⁻¹. This behavior can be explained by considering: (i) furans are more abundant in combustion processes and the higher the initial concentration, the faster the reaction rate; (ii) previous works have established that furans are more reactive than dioxins [8,9], which also generate higher reaction rates. In general, reaction rates and TOFs of more chlorinated compounds are higher than those of less chlorinated

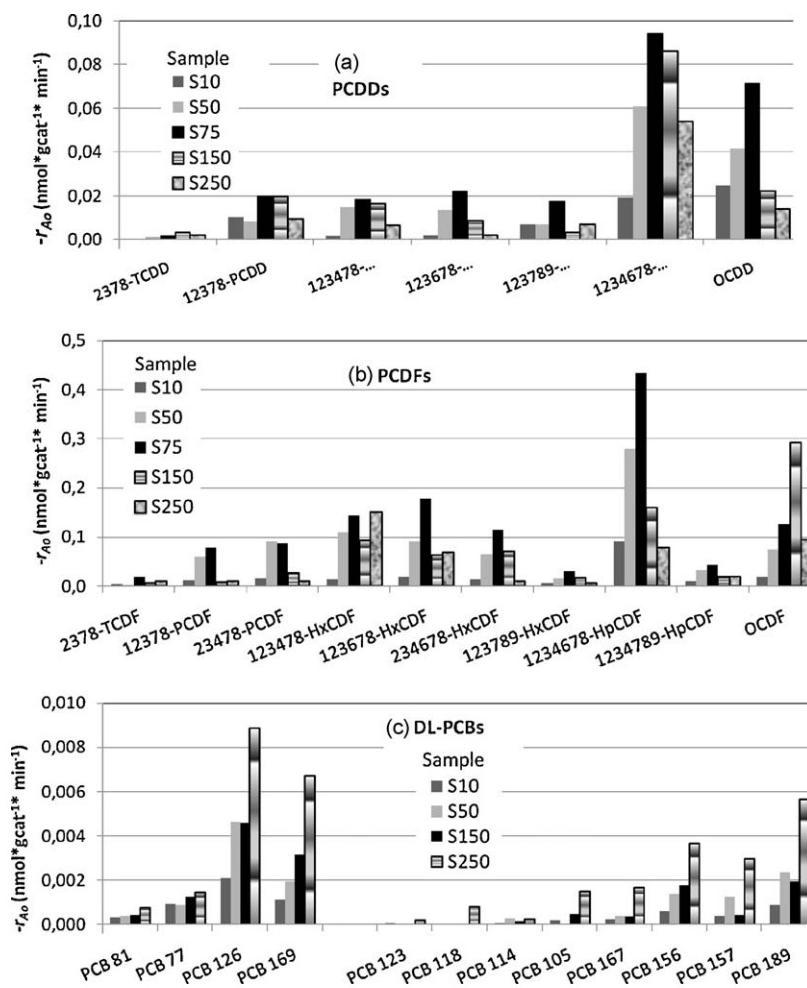


Fig. 7. Net reaction rates for (a) PCDDs, (b) PCDFs and (c) DL-PCBs using different initial concentrations. Reaction conditions: 100 mg of 2 wt.% Pd/ γ -Al₂O₃ catalyst in 20 mL of 2-propanol and 37.5 mM NaOH at 348 K.

Table 4

Turnover frequency (TOF) of PCDDs, PCDFs and DL-PCBs using different initial dioxin concentrations.

Compound	TOF \times E10 (s^{-1}) ^a				
	S10	S50	S75	S150	S250
2378-TCDD	2.20	5.11	7.19	14.05	9.27
12378-PCDD	44.93	37.01	87.02	87.09	41.26
123478-HxCDD	6.59	66.81	80.54	72.73	29.70
123678-HxCDD	9.00	59.92	97.72	37.81	8.29
123789-HxCDD	30.26	31.05	76.71	14.10	30.92
1234678-HpCDF	85.83	271.11	417.74	382.95	239.16
OCDD	109.10	184.68	317.72	99.21	61.82
2378-TCDF	17.73	7.93	77.70	25.68	41.46
12378-PCDF	49.47	262.03	346.07	38.06	44.32
23478-PCDF	65.84	397.20	381.17	118.88	42.55
123478-HxCDF	54.75	484.58	637.77	409.30	665.60
123678-HxCDF	85.73	399.76	788.47	282.85	306.11
234678-HxCDF	54.44	282.91	509.59	310.44	47.21
123789-HxCDF	21.69	66.76	129.67	75.50	25.47
1234678-HpCDF	397.24	1236.45	1925.10	706.57	342.63
1234789-HpCDF	41.27	140.58	191.18	83.11	85.55
OCDF	79.44	326.43	554.61	1296.24	417.29
PCB 81	1.26	1.83	1.89	3.38	N.D.
PCB 77	4.04	3.94	5.55	6.43	N.D.
PCB 123	0.17	0.12	0.13	0.95	N.D.
PCB 118	0.07	0.01	0.13	3.56	N.D.
PCB 114	0.17	1.25	0.62	1.07	N.D.
PCB 105	0.83	0.24	2.16	6.66	N.D.
PCB 126	9.22	20.56	20.29	39.27	N.D.
PCB 167	0.94	1.78	1.66	7.30	N.D.

Table 4 (Continued)

Compound	TOF × E10 (s^{-1}) ^a				
	S10	S50	S75	S150	S250
PCB 156	2.55	6.19	7.93	16.21	N.D.
PCB 157	1.73	5.61	2.01	13.10	N.D.
PCB 169	4.92	8.71	14.11	29.68	N.D.
PCB 189	3.79	10.40	8.56	25.02	N.D.

N.D., not determined. Reaction conditions: 100 mg of 2 wt.% Pd/ γ -Al₂O₃ in 20 mL of 2-propanol with 37.5 mM NaOH at 348 K.

^a TOF was measured using the Pd loading listed in Table 3 and a Pd dispersion of 21.3%.

ones (Fig. 7 and Table 4). Zhang et al. [31] studied the dechlorination pathway of OCDD and found a slight preference route into the chlorine of one of the 2,3,7,8 positions of the molecule. The dechlorination of toxic compounds will form congeners with no chlorine in some of the 2,3,7,8 positions, so they are non-toxic. Therefore, the dechlorination of a specific toxic compound does not necessarily generate other toxic compounds with less chlorine. Instead, it will produce other non-toxic congeners (not quantified in the present work). We previously reported the behavior of non-toxic dioxin congeners in 2-propanol [10]. Almost total degradation of all compounds was observed after 4 h and the HDC process occurred by successive degradation of more chlorinated to less chlorinated compounds. Total dechlorination of toxic and non-toxic congeners from 1245-TCDD was demonstrated by Ukitu and Miyadera [27] even though there was a redistribution of chlorinated congeners during reaction. Steric effects are also important [31] i.e. when a chlorine atom is abstracted from the OCDD molecule the hydrogen will attack the C-Cl bond from the next carbon bearing less chlorine atoms. The differences in the steric effect will produce differences in the reaction rates between congeners of the same homologue group, i.e., differences in the hexa- and hepta-chlorinated congeners. In this case, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF and PCB 126 (3,3',4,4',5-PeCB) were easily degraded (see Fig. 7 and Table 4).

Additionally, net reaction rates and TOFs of dioxins and furans vs initial concentration exhibit a parabolic profile. At low initial concentrations, net reaction rates (see Fig. 7) and TOFs (Table 4) were almost linear, showing that the degradation/formation rates increase up to a given initial value. After that the net reaction rate decreases indicating changes in this degradation/formation ratio. Therefore, the reduction of the reaction rate can be attributed to the fast formation rate of each compound, which reduces the ability of the catalyst to degrade the compound at the same rate it is formed. However, the decrease in the net reaction rate and the TOF observed for OCDD and OCDF does not correspond to their fast formation rate since they are the most chlorinated ones. TGA of used catalyst samples (Table 3) showed that the higher the initial TEQ the higher the amount and stability of carbon deposits desorbed between ΔT_2 and ΔT_3 . Therefore, the decrease of the net reaction rate may be due to the saturation and obstruction of the active phase by carbonaceous residues. On the other hand, DL-PCBs exhibit an almost linear behavior of reaction rate and TOF with initial concentration (see Fig. 7 and Table 4), probably because of their very low initial concentration (see supporting information) [52]. Therefore, the maximum in the net reaction rate/turnover frequency is an important parameter for the complete and efficient detoxification of dioxin contaminated samples.

4. Summary and conclusions

The performance of 2 wt.% Pd/ γ -Al₂O₃ for dioxin hydrodechlorination was examined using two reducing agents and different NaOH concentrations. H₂(g)/MeOH promotes Pd sintering and graphitic carbon deposition on catalyst surface. The addition of

water decreases metal sintering and dissolves soluble salts diminishing inorganic residues on the catalyst. However, hydrodechlorination activity decrease is probably due to the reduction of hydrogen solubility and low affinity of alumina (above the isoelectric point) to hydrocarbons.

Although C-OH compounds were detected on 2 wt.% Pd/ γ -Al₂O₃ samples used in the HDC of low dioxin concentrations the choice of 2-propanol as reducing agent and solvent maintains Pd particle size close to its initial values, avoids or reduces formation of Pd-C species, providing a stable environment for efficient dioxin detoxification. Nevertheless, at high dioxin concentrations large amounts of carbonaceous residues are deposited over the catalyst surface. This maybe the reason for the peak maximum observed on the net reaction rate profile of PCDDs and PCDFs for a given initial concentration. After that value the reaction rate decreases affecting the effectiveness of the detoxification system. On the other hand, there is a linear trend between net reaction rate and concentration of DL-PCBs due to their low concentration in the samples used in this study.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2009.08.016.

References

- [1] B.R. Stanmore, Combust. Flame 136 (2004) 398–427.
- [2] M.V. den Berg, L. Birnbaum, A.T.C. Bosveld, B. Brunström, P. Cook, M. Feeley, J.P. Giesy, A. Hanberg, R. Hasegawa, S.W. Kennedy, T. Kubik, J.C. Larsen, F.X. Rolaf van Leeuwen, A.K. Djien Liem, C. Nolt, R.E. Peterson, L. Poellinger, S. Safe, D. Schrenk, D. Tillitt, M. Tysklind, M. Younes, F. Waern, T. Zacharewsk, Environ. Health Prospect 106 (1998) 775–792.
- [3] E. Finocchio, G. Busca, M. Notaro, Appl. Catal. B 62 (2006) 12–20.
- [4] H. Fiedler, Chemosphere 67 (2007) S96–S108.
- [5] Z. Yang, C. Xia, Q. Zhang, J. Chen, X. Liang, Waste Manage. 27 (2007) 588–592.
- [6] G. Yuan, M. Keane, Appl. Catal. B 52 (2004) 301–314.
- [7] F.J. Urbano, J.M. Marinas, J. Mol. Catal. A 173 (2001) 329–345.
- [8] P. Tundo, C. Marques, M. Selva, Appl. Catal. B 32 (2001) L1–L7.
- [9] Y. Ukitu, T. Miyadera, Appl. Catal. A 271 (2004) 165–170.
- [10] M. Cobo, A. Quintero, C. Montes, Catal. Today 133–135 (2008) 509–519.
- [11] F. Zhang, J. Chen, H. Zhang, Y. Ni, Q. Zhang, X. Liang, Sep. Purif. Technol. 59 (2008) 164–168.
- [12] N.C. Concibido, T. Okuda, W. Nishijima, M. Okada, Tetra. Lett. 46 (2005) 3613–3617.
- [13] N.C. Concibido, T. Okuda, W. Nishijima, M. Okada, Appl. Catal. B 71 (2007) 64–69.
- [14] J.B. Hoke, G.A. Gramicci, E.N. Balko, Appl. Catal. B 1 (1992) 285–296.
- [15] C. Xia, J. Xu, W. Wu, X. Liang, Catal. Commun. 5 (2004) 383–388.
- [16] M. Cobo, J.A. Conesa, C. Montes de Correa, J. Phys. Chem. A 112 (2008) 8715–8722.
- [17] N. Krishnankutty, A. Vannice, J. Catal. 155 (1995) 312–326.
- [18] B. Aristizábal, M. Cobo, C. Montes de Correa, K. Martínez, E. Abad, J. Rivera, Waste Manage. 27 (2007) 1603–1610.

- [19] R.J. Madon, M. Boudart, Ind. Eng. Chem. Fundam. 21 (1982) 438–447.
- [20] G. Del Angel, J.L. Benitez, J. Mol. Catal. A 165 (2001) 9–13.
- [21] H.J. Kolb, L.R. Burwell, J. Am. Chem. Soc. 67 (1945) 1084–1088.
- [22] S.S. Lokras, P.K. Deshpande, N.R. Kuloor, Ind. Eng. Chem. Process Des. Develop. 9 (1970) 293–297.
- [23] C. Descamps, C. Coquelet, C. Bouallou, D. Richon, Thermochim. Acta 430 (2005) 1–7.
- [24] J.P. O'Connell, J.M. Prausnitz, Ind. Eng. Chem. Fundam. 4 (1964) 347–351.
- [25] P. Purwanto, R.M. Deshpande, R.V. Chaudhari, H. Delmas, J. Chem. Eng. Data 41 (1996) 1414–1417.
- [26] P.G.T. Fogg, W. Gerrard, Solubility of Gases in Liquids, Wiley, New York, 1991.
- [27] Y. Ukiisu, T. Miyadera, Appl. Catal. B 40 (2003) 141–149.
- [28] F.-D. Kopinke, K. Mackenzie, R. Koehler, A. Georgi, Appl. Catal. A 271 (2004) 119–128.
- [29] Y. Ukiisu, T. Miyadera, React. Kinet. Catal. Lett. 89 (2006) 341–347.
- [30] M. Mörkel, V. Kaichev, G. Rupprechter, H.-J. Freund, I. Prosvirin, V. Bukhtiyarov, J. Phys. Chem. B 108 (2004) 12955–12961.
- [31] F. Zhang, J. Chen, H. Zhang, Y. Ni, X. Liang, Chemosphere 68 (2007) 1716–1722.
- [32] G. Yuan, M.A. Keane, J. Catal. 225 (2004) 510–522.
- [33] I. Czekaj, F. Loviat, F. Raimondi, J. Wambach, S. Biollaz, A. Wokaun, Appl. Catal. A 329 (2007) 68–78.
- [34] O. Demoulin, I. Seunier, M. Naveza, C. Poleunis, P. Bertrand, P. Ruiz, Appl. Catal. A 310 (2006) 40–47.
- [35] B.S. Ahn, S.G. Jeon, H. Lee, K.Y. Park, Y.G. Shul, Appl. Catal. A 193 (2000) 87–93.
- [36] T.L. Barr, Modern Esca, the Principles and Practice of X-ray Photoelectron Spectroscopy, CRC Press, USA, 1994, pp. 25–28.
- [37] T. Taylor, J. Dykstra, J. Krzanowski, D. Domingo, D. Stampfli, J. Martin, P. Erickson, Environ. Sci. Technol. 29 (1995) 629–646.
- [38] S. Ordoñez, H. Sastre, F.V. Díez, Thermochim. Acta 379 (2001) 25–34.
- [39] B. Stasinska, A. Machocki, K. Antoniak, M. Rotko, J.L. Figueiredo, F. Goncalves, Catal. Today 137 (2008) 329–334.
- [40] M. Lenarda, E. Moretti, L. Storaro, P. Patrono, F. Pinzari, E. Rodriguez-Castellon, A. Jiménez-López, G. Busca, E. Finocchio, T. Montanari, R. Frattini, Appl. Catal. A 312 (2006) 220–228.
- [41] NIST XPS database, http://srdata.nist.gov/xps/Bind_E.asp (accessed July 13, 2008).
- [42] Lasurface XPS database, <http://www.lasurface.com> (accessed July 13, 2008).
- [43] Y. Ukiisu, Appl. Catal. A 349 (2008) 229–232.
- [44] T. Comant, A.M. Karima, V. Lebarbier, Y. Wang, F. Girgsdies, R. Schlögl, A. Datye, J. Catal. 257 (2008) 64–70.
- [45] F. He, D. Zhao, Appl. Catal. B 84 (2008) 533–540.
- [46] J. Berry, L. Smart, P. Said Prasad, N. Lingaiyah, P. Canta Rao, Appl. Catal. A 204 (2000) 191–201.
- [47] A. Barrera, M. Viniegra, P. Bosch, V.H. Lara, S. Fuentes, Appl. Catal. B 34 (2001) 97–111.
- [48] D. Kim, S. Woo, O. Yang, Appl. Catal. B 26 (2000) 285–289.
- [49] H. Aytam, V. Akula, K. Janmanchi, S. Rama Rao, K. Rao Panja, K. Gurram, J.W. Niemantsverdriet, J. Phys. Chem. B 106 (2002) 1024–1031.
- [50] E. López, S. Ordóñez, F.V. Díez, Appl. Catal. B 62 (2006) 57–65.
- [51] P. Marécot, A. Akhachane, C. Micheaud, J. Barbier, Appl. Catal. A 169 (1998) 189–196.
- [52] E. Abad, K. Martínez, J. Caixach, J. Rivera, Chemosphere 63 (2006) 570–580.